

Substituent Effects on the Oxidation and Reduction Potentials of Phenylthiyl Radicals in Acetonitrile

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The important role of sulfur compounds and in particular sulfur-centered radicals in biological systems, atmospheric chemistry, and environmental science is now well established.^{1,2} As a consequence, much attention has been paid to the study of these species, but so far no reports have appeared on the thermochemistry of sulfenium cations, RS⁺, in solution.

In this paper we wish to report on the electrochemical properties of the RS⁺/RS[•] and RS[•]/RS⁻ couples in acetonitrile, i.e., the reduction potentials of RS⁺ and RS[•].³ For the first time it has been possible to obtain thermodynamic information about a series of para-substituted phenylsulfenium cations, XC₆H₄S⁺, in solution by employing the technique of photomodulated voltammetry. Fig. 1 shows the photomodulated voltammogram of C₆H₅S[•] generated by photolysis of diphenyl disulfide with the two characteristic steady-state waves pertaining to the reduction and oxidation processes.

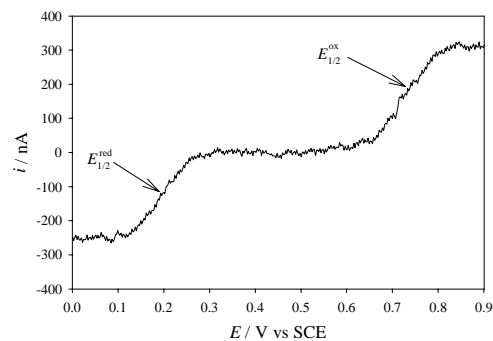


Figure 1. Photomodulated voltammogram of C₆H₅S[•] generated by photolysis of 10 mM diphenyl disulfide at a platinum electrode in 0.1 M Bu₄NBF₄/acetonitrile. The sweep rate is 0.1 V s⁻¹.

In Table 1 the half-wave potentials, $E_{1/2}^{ox}$ and $E_{1/2}^{red}$, obtained at gold or platinum minigrid electrodes are collected. Both $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ decrease as the

electron-donating power of the substituent raises, resulting in linear correlations with the Hammett substituent coefficient σ^+ with slopes ρ^+ of 4.7 and 6.4, respectively. The finding of a larger substituent effect on $E_{1/2}^{red}$ than $E_{1/2}^{ox}$ is a consequence of a corresponding development in the electron affinities and ionization potentials of XC₆H₄S[•] as revealed by quantum-chemical calculations.

Solvation energies extracted for XC₆H₄S[•] and XC₆H₄S⁺ from thermochemical cycles show the expected substituent dependency for both kinds of ions, i.e., the absolute value of the solvation energy decreases as the charge becomes more delocalized. Surprisingly, acetonitrile seems to be better in solvating XC₆H₄S⁺ than XC₆H₄S[•], even if there is a substantial delocalization of the charge in the series of phenylsulfenium cations. Since it is well known that carbocations and presumably also sulfenium ions react with acetonitrile in a Ritter reaction, it is possible that the specific solvation of the cation center by the nitrogen atom of acetonitrile is so strong that the positive charge is substantially more localized at this site than predicted by calculations.

Table 1. Half-wave potentials $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ measured for XC₆H₄S[•] at gold or platinum minigrid electrodes in 0.1 M Bu₄NBF₄/acetonitrile at 25 °C.

X	$E_{1/2}^{ox}$ ^a	$E_{1/2}^{red}$ ^a
NH ₂	0.35	-0.34
OCH ₃	0.68	-0.06
CH ₃	0.68	0.07
F	0.79	0.15
H	0.79	0.16
Cl	0.90	0.23
COOCH ₃	0.86	0.43
CN	0.98	0.42
NO ₂	<i>b</i>	0.46

^a V vs SCE. ^b No reproducible oxidation wave was observable.

References

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3) Larsen, A. G.; Holm, A. H.; Roberson, M.; Daasbjerg, K. *J. Am. Chem. Soc.* **2001**, 123, 1723.